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## POSITIVE-WORKING LITHOGRAPHIC PRINTING PLATE PRECURSOR

## [DESCRIPTION]

## 5 FIELD OF THE INVENTION

The present invention relates to a heat-sensitive positive-working lithographic printing plate precursor that requires aqueous alkaline processing.

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## BACKGROUND OF THE INVENTION

Lithographic printing presses use a so-called printing master such as a printing plate which is mounted on a cylinder of the printing press. The master carries a lithographic image on its surface and a print is obtained by applying ink to said image and then transferring the ink from the master onto a receiver material, which is typically paper. In conventional lithographic printing, ink as well as an aqueous fountain solution (also called dampening liquid) are supplied to the lithographic image which consists of oleophilic (or hydrophobic, i.e. ink-accepting, water-repelling) areas as well as hydrophilic (or oleophobic, i.e. water-accepting, ink-repelling) areas. In so-called driographic printing, the lithographic image consists of ink-accepting and ink-abhesive (ink-repelling) areas and during driographic printing, only ink is supplied to the master.

Printing masters are generally obtained by the image-wise exposure and processing of an imaging material called plate precursor. A typical positive-working plate precursor comprises a hydrophilic support and an oleophilic coating which is not readily soluble in an aqueous alkaline developer in the non-exposed state and becomes soluble in the developer after exposure to radiation. In addition to the well known photosensitive imaging materials which are suitable for UV contact exposure through a film mask (the so-called pre-sensitized plates), also heat-sensitive printing plate precursors have become very popular. Such thermal materials offer the advantage of daylight stability and are especially used in the so-called computer-to-plate method wherein the plate precursor is

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directly exposed, i.e. without the use of a film mask. The material is exposed to heat or to infrared light and the generated heat triggers a (physico-)chemical process, such as ablation, polymerization, insolubilization by cross-linking of a polymer, heat-induced solubilization, or particle coagulation of a thermoplastic polymer latex. Examples of such thermal plates, wherein also the role of surface roughness of the aluminum support is discussed, are disclosed in US 6,242,156 and EP-A 884 647.

A specific problem associated with thermal plate precursors is the limited shelf life of the coating. Especially when stored at elevated temperature, which is inevitable during transport by truck, boat, etc. the plates may show significant toning (ink-acceptance in the non-image areas).

#### SUMMARY OF THE INVENTION

It is an aspect of the present invention to provide a positive-working thermal lithographic printing plate precursor with improved shelf life. This object is realized by the material of claim 1, having the characterizing feature that a low surface roughness of the grained and anodized aluminum support unexpectedly provides an improved shelf life of the material. Specific embodiments of the invention are defined in the dependent claims.

#### DETAILED DESCRIPTION OF THE INVENTION

The support of the plate precursor of the present invention is a grained and anodized aluminum support having a hydrophilic surface that is characterized by a low surface roughness, expressed as arithmetical mean center-line roughness (Ra), sometimes also referred to as CLA (center-line average). Ra as used herein is defined in ISO 4287/1 (= DIN 4762) and references therein. Ra values reported herein have been measured according to ISO 4288 and references therein by a mechanical profile method using a contact stylus with a very thin tip (also optical profile methods are known; such optical methods systematically provide higher values than the ISO method). The apparatus used for measuring Ra was a Talysurf 10 from Taylor Hobson Ltd.

The Ra value of the hydrophilic surface of the grained and anodized aluminum support used in the material of the present invention is lower than 0.40  $\mu\text{m}$ , preferably lower than 0.30  $\mu\text{m}$  and even more preferably lower than 0.25  $\mu\text{m}$ . A grained and anodized aluminum support having a hydrophilic surface characterized by the mentioned low Ra values is briefly referred to herein as a "smooth support". The lower limit of the Ra value may be 0.05  $\mu\text{m}$ , preferably 0.1  $\mu\text{m}$ .

Graining and anodizing of aluminum lithographic supports is well known. The grained aluminum support used in the material of the present invention is preferably an electrochemically grained support. The acid used for graining can be e.g. nitric acid. The acid used for graining preferably comprises hydrogen chloride. Also mixtures of e.g. hydrogen chloride and acetic acid can be used.

The relation between electrochemical graining and anodizing parameters such as electrode voltage, nature and concentration of the acid electrolyte or power consumption on the one hand and the obtained lithographic quality in terms of Ra and anodic weight ( $\text{g/m}^2$  of  $\text{Al}_2\text{O}_3$  formed on the aluminum surface) on the other hand is well known. More details about the relation between various production parameters and Ra or anodic weight can be found in e.g. the article "Management of Change in the Aluminium Printing Industry" by F. R. Mayers, to be published in the ATB Metallurgie Journal. So the skilled person is well aware of the settings of the various parameters which are required for making a smooth surface on a grained aluminum support or for making a given anodic weight during aluminum anodization. According to the present invention, further improvements can be obtained for a given roughness Ra by forming more than 3.0  $\text{g/m}^2$  of aluminum oxide at the hydrophilic surface, a value above 4.0  $\text{g/m}^2$  being even more preferred.

The grained and anodized aluminum support may be post-treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with a sodium silicate solution at elevated temperature, e.g. 95°C.

Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with an organic acid and/or salt

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thereof, e.g. carboxylic acids, hydroxycarboxylic acids, sulfonic acids or phosphonic acids, or their salts, e.g. succinates, phosphates, phosphonates, sulfates, and sulfonates. A citric acid or citrate solution is preferred. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further post-treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulfonic acid, polyvinylbenzenesulfonic acid, sulfuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulfonated aliphatic aldehyde. It is further evident that one or more of these post-treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB-A- 1 084 070, DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909, EP-A- 537 633, DE-A- 4 001 466, EP-A- 292 801, EP-A- 291 760 and US-P- 4 458 005.

The coating provided on the support is heat-sensitive, thereby providing a plate precursor which can be handled in normal working lighting conditions (daylight, fluorescent light) for several hours. The coating preferably does not contain UV-sensitive compounds which have an absorption maximum in the wavelength range of 200 nm to 400 nm such as diazo compounds, photoacids, photoinitiators, quinone diazides, or sensitizers. Preferably the coating neither contains compounds which have an absorption maximum in the blue and green visible light wavelength range between 400 and 600 nm.

The coating may comprise one or more distinct layers. Besides the layers discussed hereafter, the coating may further comprise e.g. a "subbing" layer which improves the adhesion of the coating to the support, a covering layer which protects the coating against contamination or mechanical damage, and/or a light-to-heat conversion layer which comprises an infrared light absorbing compound.

The coating is positive-working and capable of heat-induced solubilization, i.e. the coating is resistant to the developer and ink-accepting in the non-exposed state and becomes soluble in the

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developer upon exposure to heat or infrared light to such an extent that the hydrophilic surface of the support is revealed thereby.

Preferably, the coating comprises a hydrophobic polymer that is soluble in an aqueous alkaline developer. Preferred polymers are phenolic resins, e.g. novolac, resoles, polyvinyl phenols and carboxy-substituted polymers. Typical examples of such polymers are described in DE-A-4007428, DE-A-4027301 and DE-A-4445820. In addition, the coating may comprise polymers which improve the run length and/or the chemical resistance of the plate. Examples thereof are polymers comprising sulfonamido ( $-\text{SO}_2\text{-NR-}$ ) or imido ( $-\text{CO-NR-CO-}$ ) pendant groups, wherein R is hydrogen, optionally substituted alkyl or optionally substituted aryl, such as the polymers described in EP-A 894622, 901902, 933682 and WO99/63407.

In a preferred embodiment, the coating also contains one or more dissolution inhibitors, i.e. one or more materials which reduce the dissolution rate of the hydrophobic polymer in the aqueous alkaline developer at the non-exposed areas of the coating. The dissolution inhibiting capability of the inhibitor can easily be tested by coating two samples on a support : a reference sample containing only the hydrophobic polymer and another including both the polymer (in equal amounts as the reference) as well as the inhibitor. A series of unexposed samples is immersed in an aqueous alkaline developer, each sample during a different time period. After the immersion period, the sample is removed from the developer, immediately rinsed with water, dried and then the dissolution of the coating in the developer is measured by comparing the weight of the sample before and after the development. As soon as the coating is dissolved completely, no more weight loss is measured upon longer immersion time periods, i.e. a curve representing weight loss as a function of immersion time reaches a plateau from the moment of complete dissolution of the layer. A material has good inhibiting capability when the coating of the sample without the inhibitor has dissolved completely in the developer before the sample with the inhibitor is attacked by the developer to such an extent that the ink-accepting capability of the coating is affected.

The dissolution inhibitor(s) can be added to the layer which comprises the alkali-soluble hydrophobic polymer discussed above. In

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this embodiment, the dissolution rate of the non-exposed coating in the developer is reduced by interaction between the hydrophobic polymer and the inhibitor, due to e.g. hydrogen bonding between these compounds. The dissolution inhibiting capability of the inhibitor is preferably reduced or destroyed by the heat generated during the exposure so that the coating readily dissolves in the developer at exposed areas. Such inhibitors are preferably organic compounds which comprise at least one aromatic group and a hydrogen bonding site, e.g. a carbonyl group, a sulfonyl group, or a nitrogen atom which may be quaternized and which may be part of a heterocyclic ring or which may be part of an amino substituent of said organic compound. Suitable dissolution inhibitors of this type have been disclosed in e.g. EP-A 825927 and 823327. Some of the compounds mentioned below, e.g. infrared dyes such as cyanines and contrast dyes such as quaternized triarylmethane dyes can also act as a dissolution inhibitor.

Water-repellent polymers represent a second type of suitable dissolution inhibitors. Such polymers seem to increase the developer resistance of the coating by repelling the aqueous developer from the coating. The water-repellent polymers can be added to the layer comprising the hydrophobic polymer and/or can be present in a separate layer provided on top of the layer with the hydrophobic polymer. In the latter embodiment, the water-repellent polymer forms a barrier layer which shields the coating from the developer and the solubility of the barrier layer in the developer or the penetrability of the barrier layer by the developer can be reduced by exposure to heat or infrared light, as described in e.g. EP-A 864420, EP-A 950517 and WO99/21725. Preferred examples of the water-repellent polymers are polymers comprising siloxane and/or perfluoroalkyl units. In one embodiment, the coating contains such a water-repellent polymer in an amount between  $0.5$  and  $25 \text{ mg/m}^2$ , preferably between  $0.5$  and  $15 \text{ mg/m}^2$  and most preferably between  $0.5$  and  $10 \text{ mg/m}^2$ . When the water-repellent polymer is also ink-repelling, e.g. in the case of polysiloxanes, higher amounts than  $25 \text{ mg/m}^2$  can result in poor ink-acceptance of the non-exposed areas. An amount lower than  $0.5 \text{ mg/m}^2$  on the other hand may lead to an unsatisfactory development resistance. The polysiloxane may be a linear, cyclic or complex cross-linked polymer or copolymer. The

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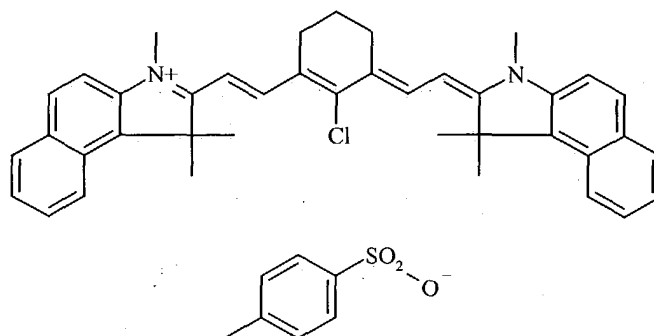
term polysiloxane compound shall include any compound which contains more than one siloxane group  $-\text{Si}(\text{R}, \text{R}')-\text{O}-$ , wherein R and R' are optionally substituted alkyl or aryl groups. Preferred siloxanes are phenylalkylsiloxanes and dialkylsiloxanes. The number of siloxane groups in the (co)polymer is at least 2, preferably at least 10, more preferably at least 20. It may be less than 100, preferably less than 60. In another embodiment, the water-repellent polymer is a block-copolymer or a graft-copolymer of a poly(alkylene oxide) block and a block of a polymer comprising siloxane and/or perfluoroalkyl units. A suitable copolymer comprises about 15 to 25 siloxane units and 50 to 70 alkylene oxide groups. Preferred examples include copolymers comprising phenylmethylsiloxane and/or dimethylsiloxane as well as ethylene oxide and/or propylene oxide, such as Tego Glide 410, Tego Wet 265, Tego Protect 5001 or Silikophen P50/X, all commercially available from Tego Chemie, Essen, Germany. Such a copolymer acts as a surfactant which upon coating, due to its bifunctional structure, automatically positions itself at the interface between the coating and air and thereby forms a separate top layer even when the whole coating is applied from a single coating solution. Simultaneously, such surfactants act as a spreading agent which improves the coating quality. Alternatively, the water-repellent polymer can be applied in a second solution, coated on top of the layer comprising the hydrophobic polymer. In that embodiment, it may be advantageous to use a solvent in the second coating solution that is not capable of dissolving the ingredients present in the first layer so that a highly concentrated water-repellent phase is obtained at the top of the coating.

Preferably, also one or more development accelerators are included in the coating, i.e. compounds which act as dissolution promoters because they are capable of increasing the dissolution rate of the non-exposed coating in the developer, which can be tested by the same procedure as described above in relation to dissolution inhibitors. The simultaneous application of dissolution inhibitors and accelerators allows a precise fine tuning of the dissolution behavior of the coating. Suitable dissolution accelerators are cyclic acid anhydrides, phenols or organic acids. Examples of the cyclic acid anhydride include phthalic anhydride,

tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxo- 4-tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride, alpha - phenylmaleic anhydride, succinic anhydride, and pyromellitic anhydride, as described in U.S. Patent No. 4,115,128. Examples of the phenols include bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,4,4'-trihydroxybenzophenone, 2,3,4-trihydroxy-benzophenone, 4-hydroxybenzophenone, 4,4',4''-trihydroxy-triphenylmethane, and 4,4',3'',4''-tetrahydroxy-3,5,3',5'-tetramethyltriphenyl-methane, and the like. Examples of the organic acids include sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphates, and carboxylic acids, as described in, for example, JP-A Nos. 60-88,942 and 2-96,755. Specific examples of these organic acids include p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, phenyl phosphate, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 4-cyclohexene-1,2-dicarboxylic acid, erucic acid, lauric acid, n-undecanoic acid, and ascorbic acid. The amount of the cyclic acid anhydride, phenol, or organic acid contained in the coating is preferably in the range of 0.05 to 20% by weight, relative to the coating as a whole.

The material can be image-wise exposed directly with heat, e.g. by means of a thermal head, or indirectly by infrared light, which is preferably converted into heat by an infrared light absorbing compound, which may be a dye or pigment having an absorption maximum in the infrared wavelength range. The concentration of the sensitizing dye or pigment in the coating is typically between 0.25 and 10.0 wt.%, more preferably between 0.5 and 7.5 wt.% relative to the coating as a whole. Preferred IR-absorbing compounds are dyes such as cyanine or merocyanine dyes or pigments such as carbon black. A suitable compound is the following infrared dye :





IR-1

The coating may further contain an organic dye which absorbs visible light so that a perceptible image is obtained upon image-wise exposure and subsequent development. Such a dye is often called contrast dye or indicator dye. Preferably, the dye has a blue color and an absorption maximum in the wavelength range between 600nm and 750 nm. Although the dye absorbs visible light, it preferably does not sensitize the printing plate precursor, i.e. the coating does not become more soluble in the developer upon exposure to visible light. Suitable examples of such a contrast dye are the quaternized triarylmethane dyes.

The infrared light absorbing compound and the contrast dye may be present in the layer comprising the hydrophobic polymer, and/or in the barrier layer discussed above and/or in an optional other layer. According to a highly preferred embodiment, the infrared light absorbing compound is concentrated in or near the barrier layer, e.g. in an intermediate layer between the layer comprising the hydrophobic polymer and the barrier layer.

The printing plate precursor of the present invention can be exposed to infrared light with LEDs or a laser. Preferably, a laser emitting near infrared light having a wavelength in the range from about 750 to about 1500 nm is used, such as a semiconductor laser diode, a Nd:YAG or a Nd:YLF laser. The required laser power depends on the sensitivity of the image-recording layer, the pixel dwell time of the laser beam, which is determined by the spot diameter (typical value of modern plate-setters at  $1/e^2$  of maximum intensity : 10-25  $\mu\text{m}$ ), the scan speed and the resolution of the exposure apparatus (i.e. the number of addressable pixels per unit of linear distance, often expressed in dots per inch or dpi; typical value : 1000-4000 dpi).

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Two types of laser-exposure apparatuses are commonly used: internal (ITD) and external drum (XTD) plate-setters. ITD plate-setters for thermal plates are typically characterized by a very high scan speed up to 500 m/sec and may require a laser power of several Watts. XTD plate-setters for thermal plates having a typical laser power from about 200 mW to about 1 W operate at a lower scan speed, e.g. from 0.1 to 10 m/sec.

The known plate-setters can be used as an off-press exposure apparatus, which offers the benefit of reduced press down-time. XTD plate-setter configurations can also be used for on-press exposure, offering the benefit of immediate registration in a multi-color press. More technical details of on-press exposure apparatuses are described in e.g. US 5,174,205 and US 5,163,368.

In the development step, the non-image areas of the coating are removed by immersion in an aqueous alkaline developer, which may be combined with mechanical rubbing, e.g. by a rotating brush. The developer preferably has a pH above 10, more preferably above 12. The development step may be followed by a rinsing step, a gumming step, a drying step and/or a post-baking step.

The printing plate thus obtained can be used for conventional, so-called wet offset printing, in which ink and an aqueous dampening liquid is supplied to the plate. Another suitable printing method uses so-called single-fluid ink without a dampening liquid. Single-fluid ink consists of an ink phase, also called the hydrophobic or oleophilic phase, and a polar phase which replaces the aqueous dampening liquid that is used in conventional wet offset printing. Suitable examples of single-fluid inks have been described in US 4,045,232; US 4,981,517 and US 6,140,392. In a most preferred embodiment, the single-fluid ink comprises an ink phase and a polyol phase as described in WO 00/32705.

## EXAMPLES

### Preparation of lithographic support 1 (comparative example)

A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 40 g/l of sodium hydroxide at 60°C for 8 seconds and rinsed with demineralized water for 2

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seconds. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 12 g/l of hydrochloric acid and 38 g/l of aluminum sulphate (18 hydrate) at a temperature of 33°C and a current density of 130 A/dm<sup>2</sup> to form a surface topography with an average center-line roughness Ra of 0.5 μm. After rinsing with demineralized water for 2 seconds, the aluminum foil was then etched with an aqueous solution containing 155 g/l of sulfuric acid at 70°C for 4 seconds and rinsed with demineralized water at 25°C for 2 seconds. The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 155 g/l of sulfuric acid at a temperature of 45°C, at a current density of 22 A/dm<sup>2</sup> to form an anodic oxidation film of 2.90 g/m<sup>2</sup> of Al<sub>2</sub>O<sub>3</sub>, then washed with demineralized water for 2 seconds and posttreated for 10 seconds with a solution containing 4 g/l polyvinylphosphonic acid at 40°C, rinsed with demineralized water at 20°C during 2 seconds and dried.

#### Preparation of the lithographic support 2 (invention)

The same procedure was used as described for lithographic support 1 with the proviso that the current density during graining and anodizing was 90 A/dm<sup>2</sup> and 30 A/dm<sup>2</sup> respectively. As a result, the Ra value was 0.2 μm and the anodic weight was 4.0 g/m<sup>2</sup>.

#### Preparation of printing plate precursor 1 and 2

The comparative printing plate precursor 1 and the printing plate precursor 2 according to the invention were produced by coating the solution defined in Table 1 onto the above described lithographic substrates 1 and 2. The coating solution was applied at a wet coating thickness of 26 μm on a coating line operating at a speed of 10.8 m/min and then dried at 135°C.

Table 1 : composition of the coating solution

	Parts (grams)
Tetrahydrofuran	209.20
Alnovol SPN452 (1)	102.02
Dowanol PM (2)	332.13
Methyl ethyl ketone	266.20
S0094 (3)	2.10
1 wt.% solution of Basonyl Blue 640 (4) in Dowanol PM	53.00
1 wt.% solution of TegoGlide 410 (5) in Dowanol PM	8.50
1 wt.% solution of TegoWet 265 (5) in Dowanol PM	21.55
3,4,5-trimethoxy cinnamic acid	5.30

(1) Alnovol SPN452 is a 40.5 wt.% solution of novolac in Dowanol PM  
(commercially available from Clariant).

(2) 1-methoxy-2-propanol from Dow Chemical Company.

(3) S0094 is an IR absorbing cyanine dye commercially available from  
FEW Chemicals. S0094 has the chemical structure IR-1 shown above.

(4) Basonyl Blue 640 is a quaternized triarylmethane dye commercially  
available from BASF.

(5) TegoWet 265 and TegoGlide 410 are both block-co-polysiloxane/  
poly(alkylene oxide) surfactants commercially available from Tego  
Chemie Service GmbH.

## 15 Evaluation and results

One part of each printing plate precursor was packaged in an  
open paper bag and stored during 7 days at ambient temperature.  
Another part of the printing plate precursor was packaged in an open  
bag and stored for 7 days at 50°C.

The printing plate precursors were then exposed on a CreoScitex  
Trendsetter 3244 operating at a drum rotation speed of 150 rpm and  
the energy on the plates was varied from 80 mJ/cm<sup>2</sup> up to 200 mJ/cm<sup>2</sup>  
with steps of 20 mJ/cm<sup>2</sup>. The plates were then processed in an Agfa  
Autolith T processor operating at a speed of 0.96 m/min using Agfa  
TD5000 developer at 25°C and RC795 as gum. Only the plates obtained  
with the optimum exposure energy were used in the evaluation, using

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a Heidelberg GT052 printing press with K+E 800 Skinnex Black (commercially available from BASF) as ink and ROTA-MATIC (commercially available from Unigraphics GmbH) as fountain. When stored at ambient temperature, both the printing plate precursor 1 and 2 had a very good lithographic behavior and printed without toning. The plate obtained from precursor 1 stored at elevated temperature showed severe toning in the non-image areas and was a useless printing plate. The plate which was obtained from the precursor 2 that had been stored at elevated temperature printed without toning.